Surface Modification of Porous Silicon by Electrochemical Reduction of Organo Halides**

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and Michael J. Sailor*

Porous silicon is a nano- to macroporous high surface area material that can be fabricated from n- and p-type silicon by chemical or electrochemical etching processes involving hydrofluoric acid. Originally it was studied for its application as an insulating material in microelectronics.[1] Later on it was discovered that many forms of porous silicon show intense photoluminescence under UV excitation,[2] which opened the possibility for applications in optoelectronics, display technologies,[3] and chemical sensing.[4] Most recently, its passive optical properties have been exploited for antireflective coatings,[5] wave guides,[6] interference filters,[7] and biosensors.[8]

Pristine porous silicon has a hydride-terminated surface that is prone to oxidation and corrosion. In recent years there has been much progress in the surface modification of porous silicon and hydride-terminated crystalline silicon with organic moieties. Covalently attached (Si–C) stable organic monolayers have been formed by cleavage of Si–Si bonds with Grignard[9] and alkyllithium reagents.[10] Similar results were obtained by a series of thermal,[11] photochemical,[12] and Lewis acid catalyzed[13] hydrosilylation reactions. Electrochemical oxidation of methyl Grignard reagents[9b] on porous silicon and electrochemical reduction of phenyldiazonium salts[14] on single-crystal silicon have been shown to yield dense monolayers of methyl and phenyl groups, respectively. In many cases the organic functionalization dramatically improves the chemical stability of porous silicon, which has spurred renewed interest in this material for sensor and display applications.

Herein we report on a fast and highly efficient electrochemical method for surface functionalization of n- and p-type porous silicon based on reductive electrolysis of alkyl iodide, alkyl bromide, and benzyl bromide species. This new method provides high surface coverage, while requiring only very short (<2 min) reaction times. Widely available mono- and bifunctional organo halide reagents with low to moderate reactivity make this method convenient to use and generally applicable.

The reductions are performed in 0.2 M to 0.4 M solutions of the organo halides in dry, deoxygenated acetonitrile or mixtures of acetonitrile and tetrahydrofuran containing 0.2 M $LiBF_4$. Alkyl bromides, which do not react as well as alkyl iodides or benzyl bromides, can be converted into the iodides in situ by replacing $LiBF_4$ with LiI as the electrolyte. Passing a cathodic current (2–10 mA cm^{-2}) for short periods of time (30–120 s) leads to high coverage of the porous silicon surface with organic species, as determined by FT-IR (Figure 1). The alkyl layers formed are stable in organic solvents and ethanolic HF, which indicates that the grafting proceeds through formation of covalent Si–C bonds.[10, 13] In the case of methyl iodide this is further established by the appearance of the Si–C stretching mode in the infrared spectrum at 766 cm^{-1}.[9b] This mode is typically not observed for alkanes with longer chain lengths.[15]

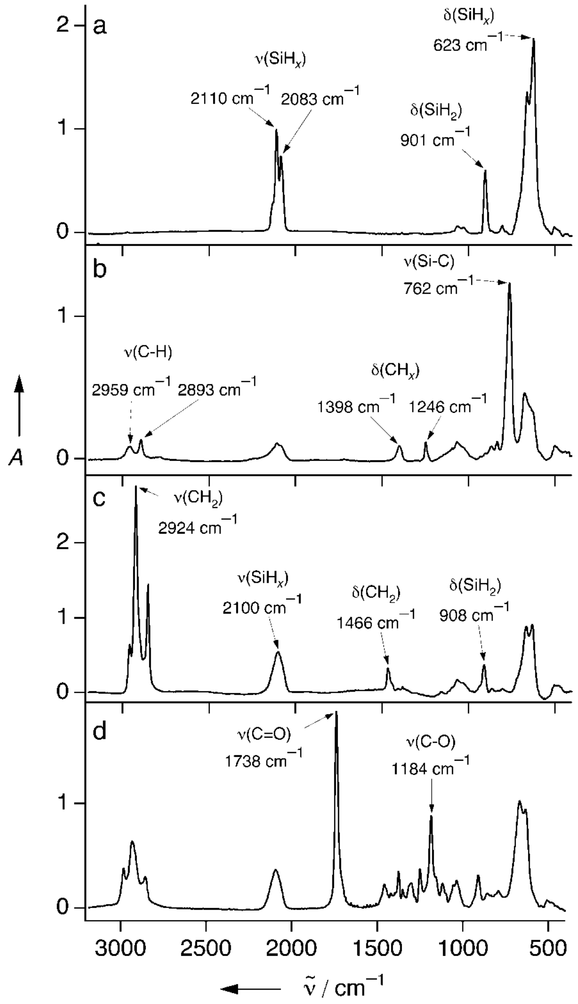

Figure 1. Transmission FT-IR spectra of p-type porous silicon a) before and after derivatization with: b) methyl iodide, c) dodecyl iodide, and d) ethyl 6-bromohexanoate. Absorbance intensities *A* are normalized to the $\tilde{\nu}$(SiH) band at 2116 cm^{-1} measured before derivatization. Thin film optical interference effects that contribute to a sinusoidal baseline have been subtracted mathematically. Reaction conditions were: b) 0.4 M CH_3I, 0.2 M $LiBF_4$, acetonitrile, 2 min; c) 0.4 M $C_{12}H_{25}I$, 0.2 M $LiBF_4$, 1:1 acetonitrile/THF, 30 s; d) 0.25 M $C_8H_{15}O_2Br$, 0.2 M LiI, acetonitrile, 45 s. Cathodic current density was 10 mA cm^{-2} for all samples.

The integrated intensity of the Si–H stretching vibrations located at approximately 2120 cm^{-1} decreases substantially with increasing alkyl coverage (Figure 2). This suggests that the reduction produces alkyl or benzyl radical species that

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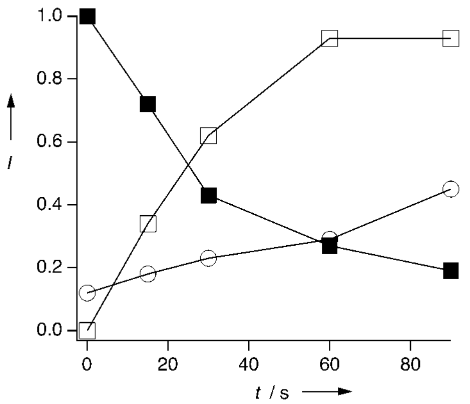
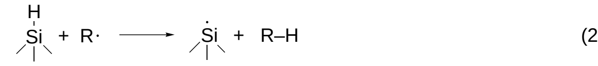


Figure 2. Plot of the integrated absorbance intensities I of the $\tilde{\nu}$(Si–H$_x$) (■, 2300–2000 cm^{-1}), $\tilde{\nu}$(Si–C) (□, 820–720 cm^{-1}), and $\tilde{\nu}$(Si–O) (○, 1200–950 cm^{-1}) vibrations as a function of methyl iodide reduction time (the same conditions as in Figure 1 were used). The intensity of the $\tilde{\nu}$(Si-C) absorbance becomes constant after 60 s, which indicates that the functionalization reaction is complete within this time. The $\tilde{\nu}$(Si–H$_x$) absorption intensity continues to decrease as the $\tilde{\nu}$(Si–O) absorption continues to increase during the course of the reaction.

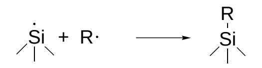
then react with the hydride surface as outlined in Equations (1) and (2).

$$R\text{–}X + e^- \rightleftharpoons [R\text{–}X]^{-\cdot} \longrightarrow R\cdot + X^- \quad (1)$$

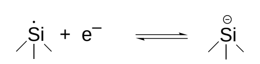


$$\overset{\mathrm{H}}{\mathrm{Si}} + R\cdot \longrightarrow \dot{\mathrm{Si}} + R\text{–}H \quad (2)$$

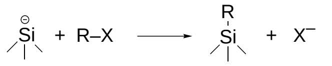
The derivatization step may occur either by direct reaction of the surface silicon radical with an alkyl- or benzyl radical [Eq. (3)], or by reduction of the silicon radical to the anion followed by nucleophilic attack on the organo halide [Eqs. (4) and (5)]. Solution-based silicon radicals are known to abstract halogen atoms from organo halides, to produce Si–X and the corresponding organic radical.[16] If this reaction occurs on the porous Si surface it is expected that under the conditions of the electrochemical experiment the Si–X species would be reduced to a silicon anion [Eq. (6)].



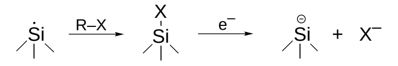
$$\dot{\mathrm{Si}} + R\cdot \longrightarrow \overset{\mathrm{R}}{\mathrm{Si}} \quad (3)$$



$$\dot{\mathrm{Si}} + e^- \rightleftharpoons \overset{\ominus}{\mathrm{Si}} \quad (4)$$



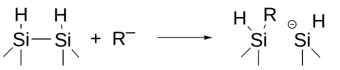
$$\overset{\ominus}{\mathrm{Si}} + R\text{–}X \longrightarrow \overset{\mathrm{R}}{\mathrm{Si}} + X^- \quad (5)$$



$$\dot{\mathrm{Si}} \xrightarrow{R\text{–}X} \overset{\mathrm{X}}{\mathrm{Si}} \xrightarrow{e^-} \overset{\ominus}{\mathrm{Si}} + X^- \quad (6)$$

It is also plausible that a minor fraction of the carbon radicals are further reduced to carbanions, which then react with the porous silicon surface by cleavage of Si–Si bonds (or Si–X bonds), similar to Grignard or alkyllithium reagents ([Eqs. (7) and (8)] followed by equation (5)).[9a, 9c, 10]

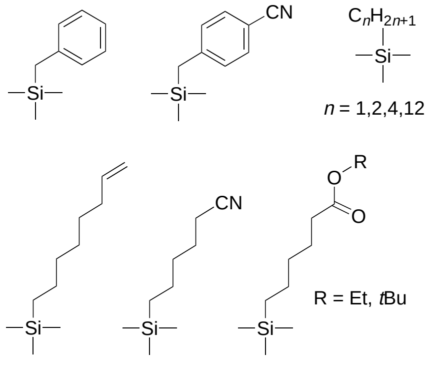
$$R\cdot + e^- \rightleftharpoons R^- \quad (7)$$



$$\overset{\mathrm{H}}{\mathrm{Si}}\text{—}\overset{\mathrm{H}}{\mathrm{Si}} + R^- \longrightarrow \overset{\mathrm{H\ R}}{\mathrm{Si}}\ \ \overset{\ominus\ \mathrm{H}}{\mathrm{Si}} \quad (8)$$

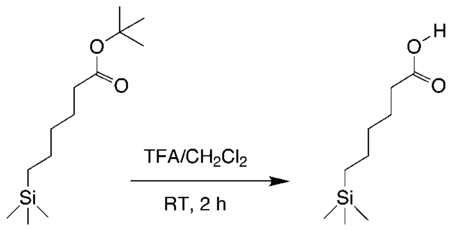
The grafting process is complete within 60–90 seconds (at a cathodic current density of 10 mA cm^{-2}) for all the organo halides studied. Longer reduction times do not lead to increased coverage, but they do lead to a higher degree of oxidation as reflected by the growth of a $\tilde{\nu}$(SiO) vibrational band at 1100–1050 cm^{-1} (Figure 2).

Even though the reduction of organo halide species requires strongly negative potentials in the range of –1.2 V to –1.8 V (versus the saturated calomel electrode (SCE)), the electrochemical procedure described here is compatible with a surprising number of functional groups (Scheme 1). Particularly useful for further derivatizations are *tert*-butyl esters.



Scheme 1. Functional groups that have been grafted onto porous silicon by electrochemical reduction of organo halides.

The ester functionalized surfaces were converted into the free acids at room temperature by addition of a mixture of trifluoroacetic acid (TFA) and dichloromethane [Eq. (9)]. Interestingly, we were unable to graft phenyl groups onto the surface of porous silicon. Reduction of phenyl iodide causes extensive oxidation and leads to very little grafting.



(9)

The photoluminescence (PL) of porous silicon samples, which is readily observable before derivatization, is eliminated entirely upon reductive derivatization with all of the alkyl iodides studied. This is presumably a consequence of residual iodo species (as detected by energy dispersive X-ray analysis, EDX), which can effectively quench the photoluminescence of porous silicon.[17] Attempts to remove these species or to recover the PL were unsuccessful. Derivatizations with alkyl bromides and benzyl bromide lead to only partial loss of the PL (with LiBF$_4$ as electrolyte). Approximately 30% of the initial PL is retained after functionalization with the bromide reagents; subsequent rinsing of the samples with ethanolic HF results in restoration of the PL to 70–90% of the original intensity.

The surface derivatization method described here is not limited to porous silicon, but is also applicable to hydride-terminated crystalline silicon. Reduction of butyl iodide on n-type crystalline silicon leads to an organic layer that is stable in boiling chloroform, aqueous ethanolic HF and 0.1м KOH as demonstrated by the difference between contact angles measured on derivatized and nonderivatized surfaces, respectively.

Experimental Section

All reagents were obtained from commercial sources and used as received. *tert*-butyl 6-bromo-hexanoate was prepared from 6-bromohexanoic acid and *tert*-butanol according to the literature.[18] Acetonitrile and THF were dried and distilled prior to use. Solutions of organo halides containing electrolyte were freeze-pump-thaw degassed three times to remove traces of oxygen and stored under nitrogen.

Porous silicon samples were prepared from n-type (P-doped) and p-type (B-doped) silicon wafers with a (100) orientation and with a resistivity of approximately 1 Ωcm. Porous silicon samples with areas of 0.25 cm^2 were etched in 48% aqueous HF/EtOH (1/1) for 2 min at a current density of 40 mA cm^{-2}. Both n- and p-type wafers were illuminated during the etching procedure[19] with a 300-W tungsten lamp adjusted to an intensity of approximately 100 mW cm^{-2} to produce luminescent samples. The porous layers were approximately 3–5 μm thick (determined by scanning electron microscopy). After the etching process the samples were rinsed with ethanol and dichloromethane, dried under a stream of nitrogen, and evacuated in a one- or two-compartment electrochemical cell equipped with a platinum auxiliary electrode and in some cases a Ag/AgBr pseudo-reference electrode. Crystalline silicon samples (n-type) were degreased in boiling chloroform. The native silicon oxide layer was removed immediately before the derivatization step by soaking in 2% aqueous HF.

Derivatization was performed by passing a cathodic current (usually 10 mA cm^{-2}) through 1–2 mL of the organo halide solution that was previously added to the porous silicon sample. The p-type porous silicon samples were illuminated with 200 mW cm^{-2} white light to supply sufficient photocurrent. After derivatization the solution was removed and the sample rinsed sequentially with glacial acetic acid, ethanol, and dichloromethane.

Derivatization of single-crystal silicon samples was monitored indirectly by comparing contact angles (water droplets) measured on derivatized and nonderivatized areas, respectively. Prior to the measurement the entire sample was immersed in boiling chloroform (15 min) and in 48% aqueous 1/1 HF/EtOH (2 min) to remove any adsorbed or Si–O bonded species, and then dipped in 0.1м aqueous KOH to render the nonderivatized, silicon hydride terminated areas hydrophilic.

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S-Cylindrophanes: From Metal Tweezers to Metal Sandwiches**

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Over the years effort has been directed at attempts to produce cyclophane-based macrobicycles **1** for the purpose of metal ion encapsulation.[1] In cases where the metal–arene core structure is intrinsically stable, such as in the ferrocenophanes, this has been a straightforward matter of building the cage around the metal. Where weaker interactions would be involved, however, the receptor must be put together first and the metal introduced later. This is the case when the aromatic system is benzene. Although the basic proposition is a simple one—that is, to create a cavity between two benzene rings and involve the π systems in the binding of a metal—its realization

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